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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This is the Final Report for this grant and includes major results along with publications. Some results noted include preparation and study of a low band-gap transparent conducting polymer, poly[1,4-bis(2-heteroaryl)-p-phenylenes], electroactive transition metal containing polymers and conducting polymer composites. In addition, many studies dealing with ion transport upon redox switching of these electroactive polymers have been carried out and new probes to monitor these ion fluxes have been developed. A highly efficient polypyrrole platinum "nano-composite," with useful catalytic properties has also been developed. Accurat theoretical and computational techniques, along with a modified Extended Hückel band structure procedure, have been developed.

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FINAL REPORT

Electronic and Ionic Transport in Processable Conducting Polymers

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Electronic and Ionic Transport in Processable Conducting Polymers

The following is a summary of some of the important results which we have achieved and studies which have been done over the past three years.

1) Poly(2,3-dihexylthieno[3,4-b]pyrazine), with a band-gap of 0.95 eV and a doped conductivity of 3.6×10^{-2} S cm^{-1}, has been prepared and it went from opaque blue-black to transparent light yellow upon doping.
2) Bis(2-furanyl) phenylene polymers have been synthesized and shown to exhibit substituent independent conductivities due to low steric interactions along the conjugated chain.
3) Dual ion transport has been induced during electrochemical switching using conducting polymer bilayers.
4) Water soluble polybenzimidazole (PBI) based polyelectrolytes have been synthesized by PBI derivatization reactions.
5) A chain-growth polymerization mode has been discovered for the electropolymerization of pyrrole in aqueous ClO_4^-, BF_4^- and PF_6^- electrolytes.
6) Poly(1,3-cyclohexadiene-*alt*-2-fluoroacrylonitrile) has been synthesized, shown to be an alternating copolymer and exhibits improved thermal stability over its chloroacrylonitrile analog.
7) Symmetrically substituted poly[1,4-bis(2-thienyl)-2,5-dialkoxyphenylenes] have been shown to be more highly ordered (semi-crystalline) and to exhibit higher conductivities than their amorphous, unsymmetrically substituted analogs.
8) EPR studies of poly[1,4-bis(2-thienyl)-2,5-dialkoxyphenylenes] during redox switching has shown a rare stabilization of a polaronic state.
9) Composites of electrically conducting metal tetrathiooxalates and poly(vinyl alcohol) with high mechanical durability have been prepared.
10) Processable and electroactive nickel bis(dithiolene) containing polycarbonates and polyurethanes have been shown to serve as near-infrared absorbing films.
11) Fibers and films of blends of poly(3-decylthiophene)with polyethylene, prepared in collaboration with Hoechst-Celanese Research Center, showed no diminution in electrical conductivity compared with pure poly(3-decylthiophene) but spinning properties were vastly improved.
12) New families of in situ probes for monitoring ion fluxes across electrode/electrolyte interphases were developed.
13) Highly efficient polypyrrole/platinum "nanocomposites" for electrocatalysis and fuel cell applications were developed. (patent pending)

14) A new voltammetric method for characterizing chemically-synthesized conducting polymers was developed. (patent pending)
15) The electrochemical quartz crystal microgravimetry technique for the study of conducting polymers was refined.
16) A better understanding of ion transport in "self-doped" conducting polymer composites was achieved.
17) Accurate theoretical techniques for the evaluation of the relative stability of the quinoid and aromatic forms of conjugated polyheterocycles was developed.
18) Efficient and practical computational techniques for performing conformational analyses on conjugated polyheterocycles, including accurate estimates of the backbone twist angles, which are extremely important for the prediction on band gaps, was developed.
19) A modified Extended Hückel band structure procedure which yields remarkably accurate band gaps in these systems was developed.

The following is a listing of the journal publications and technical reports which have emanated from the grant.

Papers Published in Refereed Journals

1) Nayak, K. and Marynick, D. S. "The Interplay between the Geometric and Electronic Structures of Polyisothianaphthene Polyisonaphthothiophene, Polythieno(3,4-b)pyrazine and Poly(3,4-b)quinoxaline", *Macromolecules* **1990**, *23*, 2237-2245.

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17) Panchalingam, V. and Reynolds, J. R. "Poly(1,3-cyclohexadiene-*alt*-α-fluoroacrylonitrile): Synthesis and Structural Analysis of a New Alternating Copolymer", Technical Report No. 34, Grant No. N00014-90-J-1320 DARPA/ONR, October 21, 1991.

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